

The Stability, Mixed-Conductivity and Applications of Cation-Doped Yttria-Stabilized Zirconia (YSZ)

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Yttria-stabilized zirconia (YSZ) electrolytes have a unique combination of high oxygen-ion conductivity and high electrochemical stability at elevated temperatures. Their electrochemical applications in oxygen sensors and solid-oxide fuel cells are well known. However, there is increasing interest in the development of mixed-conducting YSZs for electrode and membrane applications such as fuel cells, sensors and oxygen-separation membranes. In this paper, the criteria and procedures used to introduce mixed-valent cations into YSZ are first reviewed. Then the effect of the doped cations on the electronic and oxygen-ion conductivities is summarized. Lastly, selected examples of the enhancement of the electrochemical behavior in cells with YSZ-based mixed conductors are reviewed.

1. Effect of Cation Valence and Size on Solubility Limits and the Stability of the YSZ Cubic-Fluorite Structure

Electronic conductivity is introduced into YSZ by the dissolution of oxides having a multivalent cation. Oxides having significant solubility and introducing electronic conductivity include ceria (CeO_2), praseodymia ($\text{PrO}_{1.5}$), terbia (Tb_2O_3) and titania (TiO_2). The extent of their solid solubility in cubic YSZ is strongly influence by the valences and sizes of the multivalent cations. The valence of the multivalent-valent cation and the associated electronic conductivity in mixed-conducting YSZ can vary with oxygen partial pressure and temperature.

2. Type of Electronic Conductivity in Cubic YSZ and Its Influence on the Oxygen-Ion conductivity

Multivalent-cation dopants, such as Ce, Pr, Tb, and Ti, introduce electronic conductivity into YSZ. These can be separated into two groups: those that introduce p-type electronic conductivity in the higher oxygen-pressure environments (e. g. air), and those that introduce n-type electronic conductivity in the lower oxygen-pressure (e.g. fuel gas) environments. The minority valence state of the multivalent cation determines whether the electronic conductivity is p-type or n-type.

Conductivity and blocking-electrode measurements have been used to determine the significance of the p- and n-type conductivity in YSZ doped with multivalent cations at temperatures between 600 and 1000°C. The predominate electron-conduction mechanism is electron hopping between the multivalent cations. The magnitude of the electronic conductivity introduce by specific multivalent cations into YSZ varies with the composition of the dopant cation.

It is also important to note that the introduction of electronic conductivity can degrade the oxygen-ion conductivity. For example, if the electronic conductivity is established by a cation whose predominate valence is 3+, the oxygen-ion conductivity of YSZ can decrease. This is due to the increased oxygen-vacancy concentration necessary to compensate for the placement of the 3+ cations on a Zr^{4+} cation sites.

3. Enhancement of the Electrochemical Performance of Cells with Mixed-Conducting YSZ

Enhancements of the electrochemical cell behavior using YSZ-based mixed conductors are cited. For example, the cathodic and anodic overpotentials in YSZ-electrolyte cells with doped-YSZ mixed conductivity have been determined [1 – 6]. The current-interruption technique with three-electrode cells has been used at temperatures between 700 and 950°C. Results indicated that doped-YSZ mixed-conductors can reduce significantly overpotential losses and enhance the performance of electrochemical cells.

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References

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